Durable Catalysts for Fuel Cell Protection during Transient Conditions

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3M

DOE/3M Award DE-EE0000456

2014 DOE Hydrogen and Fuel Cells Program
and
Vehicle Technologies Program Annual Merit Review

Washington DC, June 17, 2014

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Overview

Barriers
Electrode Performance: Catalyst durability under
- start-up & shut-down (SU/SD) estimated at ~ 4,000 events and
- cell reversal (CR) estimated at ~ 200 events

Timeline
- Project start date: August 1, 2009
- Project end date: June 30, 2014
- Percent complete: >90% (03/2014)

3M (Project lead)

Partners/Collaborators
- AFCC (Subcontractor)
  - Independent evaluation, Short-stack testing, Ex-situ/in-situ characterization, Integration, Fundamental understanding
- Dalhousie University (Subcontractor)
  - High-throughput catalyst synthesis and basic characterization
- Oak Ridge National Lab (Subcontractor)
  - STEM Characterization
- Argonne National Lab (Subcontractor)
  - XAFS, Stability Testing, Selective ORR Inhibitor

Budget
Total: $ 5,382,165
- Contractor Share: $ 1,156,433
- DOE Share: $ 4,625,732
  (additional $ 400K to ORNL)

Funds spent (3/2014): $ 5,121,459
(including ORNL cost-share)
Objectives and Relevance

**Objective:**
Develop catalysts that will enable PEM fuel cells systems to weather the damaging conditions in individual fuel cells during transient periods of fuel starvation, thus making it possible to satisfy 2015 DOE targets for catalyst performance, PGM loading, and durability.

**Relevance:**
Fuel starvation could result in high positive voltages at the cathode during start-up/shut-down (SU/SD) or, at the anode, during cell reversal (CR). This project will develop a catalyst that favors the oxidation of water over the dissolution of platinum and carbon at voltages encountered beyond the range of normal FC operation and beyond the thermodynamic stability of water (> 1.23 V).

**Approach:**
Materials based, as such, protection is provided from within the MEA and is therefore always “ON”.

**Implementation:**
Via two catalyst material concepts:

1. Catalysts with high oxygen evolution reaction (OER) activity
   - At the cathode for SU/SD
   - At the anode for cell reversal

2. Anode catalysts with low oxygen reduction reaction (ORR) activity for SU/SD

**Evaluation:**
- Lab-scale for material development (50 cm²)
- Scale-up to full size CCMs (>300 cm²)
- Short stack integration and “real life” testing with AFCC test protocols (specifics on next slide)
Approach/Milestones

<table>
<thead>
<tr>
<th>Task 1: OER Active</th>
<th># of Cycles</th>
<th>PGM (mg/cm²)</th>
<th>End Voltage (V)</th>
<th>ECSA Loss (%)</th>
<th>Status/Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>SU/SD (Cathode)</td>
<td>(&gt; 5,000)</td>
<td>0.095</td>
<td>1.60</td>
<td>12%</td>
<td>Achieved 09/2011</td>
</tr>
<tr>
<td></td>
<td>(&lt; 0.090)</td>
<td>1.60</td>
<td>10%</td>
<td></td>
<td>Achieved 01/2012; End Voltage: 1.48 V</td>
</tr>
<tr>
<td></td>
<td>(&lt; 0.088)</td>
<td>1.45</td>
<td>10%</td>
<td></td>
<td>Achieved 11/2012; End Voltage: 1.44 V</td>
</tr>
<tr>
<td>Cell Reversal (Anode)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2011</td>
<td>200</td>
<td>0.050</td>
<td>2.00</td>
<td></td>
<td>Achieved 09/2011</td>
</tr>
<tr>
<td>Go/No Go</td>
<td>(&lt; 0.045)</td>
<td>1.80</td>
<td>10%</td>
<td></td>
<td>Achieved 01/2012; End Voltage: 1.65 V</td>
</tr>
<tr>
<td>2013</td>
<td>200</td>
<td>0.037</td>
<td>1.75</td>
<td>10%</td>
<td>Achieved 11/2012; End Voltage: 1.62 V</td>
</tr>
</tbody>
</table>

Task 2: Suppression of ORR (Anode)

| Go/No Go | A factor of 10 in the kinetic region | Achieved 01/2012; A factor > 100 |
| 2013     | A factor of >100 in the kinetic region | Achieved 02/2013; A factor > 1,000 |

Task 3: Scale-up

| 2012     | Scale up to full size cells (> 300 cm²) | Evaluated in 2012: 10 short stacks |
| 2013     | “Real life” evaluation – AFCC | 9 x (3 or 15)-cells short stacks |

2013 - 14 Tasks: Mitigating the impact of gas switching on the OER catalyst stability

- Root cause analysis and working hypothesis
- OER catalysts modification: composition and construction parameters
- Fundamentals of modified OER catalysts activity and stability

Milestone: After 200 Gas Switches(GS) 10 hours at – 0.2 A/cm² at < 1.7 V with < 35 mg/cm² PGM

### AFCC Stack Testing
(based on 3M made CCMs)

<table>
<thead>
<tr>
<th>Task #1 Item</th>
<th>Milestone Deliverable</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Performance and reversal testing of NSTF anode with very low and very high OER loading (3 X 15 cell short stacks &amp; 3X3 cell short stacks).</td>
</tr>
<tr>
<td>b</td>
<td>CO tolerance and SU/SD testing of one of the stacks from “a”</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Task #2 Item</th>
<th>Milestone Deliverable</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Performance testing and SU/SD testing of one 15 cell stack with highly selective anode design</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Task #3 Item</th>
<th>Milestone Deliverable</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Baseline performance testing of a 15 cell stack with a dispersed anode design</td>
</tr>
<tr>
<td>b</td>
<td>Testing results data for 4 x 15 short cell stacks. Tests include: Performance (hot operating conditions, normal operating conditions, warm-up operating conditions). Hydrogen concentration sensitivity</td>
</tr>
<tr>
<td>c</td>
<td>One reversal tolerance test based on a stack from ‘b’</td>
</tr>
</tbody>
</table>

### Main Findings
- Good HOR activity down to **0.02 mg/cm² Pt** (under most conditions)
- >**0.015 mg/cm² Ir** required for satisfactory reversal performance
- Reversal tolerance loss after **gas switching from air to hydrogen**
Mitigating the Effects of Hydrogen – Air

1. Root cause hypothesis
   1. High electrode potential: - the GS does not provoke a high anode potential (≈ 1 V under air)
   - OER catalyst is stable up to 1.75 V.
   2. Hydrogen-air direct recombination on the anode catalyst:
      • On platinum the reaction is vigorous: produces heat and a variety of radicals
      • OER-Pt/NSTF construct provides atomic proximity of OER catalyst to Pt reaction sites
      • Admixed IrRu catalyst with dispersed Pt did not lose much of its performance due to GS

2. Diminishing gas switching impact: The approach
   The strategy
   1. Slow down the rate of H₂ + O₂ reaction by blocking Pt active sites to inhibit O₂ adsorption
   2. Distance Ir from Pt - place interlayer between Pt and Ir
   The concept
   - material-based as is the OER modified anode
   - fits into the philosophy of a protection from within the MEA and as such is always ‘on’
   Materials requirements
   - stable when exposed to high potentials during cell reversal
   - implementing an amount sufficient to inhibit the H₂ – O₂ reaction without compromising HOR
   - manufacturing via processes compatible with the existing OER anode fabrication
   - adding little, preferably not at all, to the PGM loading

Four ‘refractory metals’ as stabilizing layer

- Inexpensive compared to the PGMs
- Can be sputter-deposited in vacuum
Experimental Protocol

1. Anode Evaluation + Conditioning (14 TC)
2. ORR performance
3. Low current reversal pulses (12 & 44 mA/cm², 60 & 30 sec, 20 pulses)
   - 30 sec, -1 mA/cm²
4. High current reversal pulses (200 mA/cm², 15 sec, 200 pulses)
   - 20 sec, -1 mA/cm²
   - DOE requirement, 1.7 V
5. 200 Gas Switch (GS) and Load Cycle (LC)
   - “Real life” degradation experience
   - GS Potentials
     - 280 SCCM Air, 20s
     - 800 SCCM H₂, 15s
   - LC Potentials
     - 0.7 A/cm², 10 s
     - 1.5 A/cm², 30 s
6. Most rigorous test: combined/consecutive LC + GS (LCGS)
7. High current reversal hold (200 mA/cm²)
   - Extended reversal durability (2.2 V, up to 10 hrs)

Extended tests include:
- 2,000 LCGS
- Counter Electrode: Air
- Extended Reversal time >10 hrs

¹70 °C, A/C N₂/1% H₂@1,000 SCCM, 110% RH
²Evaluation of HOR performance and ECSA are made between most step.
CCM Evaluation

- **Catalysts Depositions** (Andy, Armstrong, 3M)
  (>60, 5 ft each)
- **CCM Testing** (Jimmy Wong, Theresa Watschke, 3M)
  (>200, 50-cm² FC)
Addition of only 50 Å Zr already benefits cell reversal

Best reversal durability is around 250 Å Zr, 10 hours under the 1.7 V target

Durability starts to suffer at >300 Å Zr

Note: Graphs presented are representative of multiple CCMs

OER Activity increases with thicker Zr layer (up to 300 Å Zr)

Pt surface area follows similar trend
The Impact of Zr Layer Location

Reversal durability after GS of 20 µg/cm² Pt + 15 µg/cm² Ir

- Zr placed on same anode substrate in 3 different positions: **Top** (PtIrZr), **Sandwich** (PtZrIr), **Mixed** (PtZr(150 Å) IrZr Mixed(100 Å))
- Zr Thickness layer: 250 Å (100 Å and 150 Å for comparison)

- The placement of Zr in the Pt, Ir, Zr catalyst is crucial
- Zr is most effective as interlayer between Pt and Ir, the ‘S’ construction
- Zr had very little effect as a top layer, ‘T’ construction
- ‘Mixed’ Zr + Ir layer construct did not add any benefits
- Separating Pt from Ir mitigates substantially the gas switch impact.

![Graph showing 200 mA/cm² Reversal](chart)

- 200 mA/cm² Reversal: 20 µg/cm² Pt + 15 µg/cm² Ir
- Zr Thickness layer: 250 Å (100 Å and 150 Å for comparison)
**Comparison of Zr, Hf, Ti, Ta as Additives**

- best of each class is displayed -

- **Zr** and **Hf** produce superior reversal durability and OER activity (within the DOE target).

- **Ta** best reversal is with only 25 Å layer

- **Ti** inhibits the OER

- Hydrogen Oxidation Reaction (HOR) is within the margin of error
Impact of Combined Zr and Hf Interlayer
- tested under combine consecutive Load Cycle and Gas Switching (LCGS) -

- Combined Zr and Hf, Reversal tolerance after 200 LCGS cycles increases above single additives.
- Effect of Placement of Zr and Hf in respect to each other within the interlayer is minor
- Wide range of Zr/Hf ratios - 90/10 to 10/90 produces acceptable reversal tolerance.
- Pt surface area as well as OER activity are enhanced by Zr & Hf over baseline.

The wide range of Zr/Hf ratios and constructs within the separating layer:
- Eliminates the needs for use of ultrapure Zr and Hf in respect to each other
- Allows a wide processing window
‘Real Life’ Application:

**Testing with Cathode under AIR**

- **Testing extended beyond 10 h milestone**

![Graph](image)

- Baseline 120/5
- 225Zr/25Hf, CE: Air

**Impact of extended LCGS cycling**

**CR Durability after 2000 LCGS**

![Graph](image)

- Baseline
- Hf 200 GS
- Hf 200 LCGS
- Hf 2000 LCGS

During reversal the cathode is under air rather than hydrogen (used in most of our evaluation on the counter electrode).

- There is no significant difference in the reversal durability, other than potential shifts, whether there was hydrogen or air on the counter electrode.

- The anode can endure an **additional 2 – 4 hours beyond the milestone 10 hours** at 1.7 V voltage limit and up to an additional 10 hours to the “real life” 2.2 V limit.

- With ten times more LCGS pulses, **2000**, the reversal tolerance is decreased by a factor of 3, yet to a respectable **3.3 hours**.
Fundamental Evaluation

- **XPS** (Liliana Atanasoska, 3M)
- **Cyclic Voltammetry** (Dennis van der Vliet, 3M)
- **EXAFS** (Debbie Myers, A. Jeremy Kropf, ANL)
- **STEM** (David Cullen, ORNL)
XPS: Ir, Zr, and Pt Concentrations and Oxide level as a Function of Zr Thickness

- As received samples -

- XPS data are in agreement with having Zr between Pt and Ir
- Ir level is constant consistent with its position on the surface
- Pt signal attenuates with the increase of Zr layer thickness

Zr 3d: Zr metal (~80%), Zr sub-oxide and ZrO₂
O 1s: Growth of oxide oxygen
No significant change in Pt 4f and Ir 4f core level spectra

Zr 3d and O 1s Core level spectra

Hf deposit contains 3% at. of Zr
Stability of PtZrIr: Blank Cyclic Voltammetry
- Evaluated as CCMs -

- Larger PtOx reduction peak with Zr
  - Indicates more Pt oxide is formed
- IrOx reduction at slightly lower potential
  - Stabilization of iridium oxide
  - \( H_{\text{upd}} \) is blocked by the oxide.
  - Blockage is reversible
- Extensive scanning to 1.45 V irreversibly blocks the \( H_{\text{upd}} \)
  - this causes anode performance loss

Hf exhibits irreversible \( H_{\text{upd}} \) blockage, different than Zr
- Stable in GS, but performance loss

Stabilizing the Pt and Ir oxides is paramount in increasing OER catalyst durability.
More Pt than Ir is lost from anode during conditioning of Pt-Ir and Pt-Zr-Ir

Ir was lost from anode without Zr interlayer

With Zr interlayer, anode retained Ir

Supports hypothesis that Zr interlayer is maintaining anode activity by preventing loss of Ir
• Z-contrast STEM image of PtZrIr whisker surface in CCM before testing

• Ir, Zr(oxide), and Pt regions are labeled.
  • Interconnected network of Pt particles with regions of bare perylene-red
  • Darker Zr(oxide) layer between Pt and Ir
  • Bright Ir “islands” on top of Zr layer.

• Green arrows indicate regions where Ir and Pt layers appear to be in physical contact with each other.
STEM: Catalyst Modifications during Testing

PtZrIr

GS

After cell reversal

Ir layer becomes more like nanoparticles. Very limited Ir dissolution

Significant Ir dissolution, but Ir still observed on top of Zr layer

Ir layer becomes more like nanoparticles. Very limited Ir dissolution

Complete or nearly complete Ir dissolution

Additional Ir dissolution observed

Complete or nearly complete Ir dissolution

20 nm

20 nm

20 nm

20 nm
200 mA/cm²

Ir on surface throughout test, significant loss only observed after cell reversal, still see some Ir on surface

Ir losses begin at 200 mA, continue during GS and Cell Reversal, complete or nearly complete loss observed
Differences in Ir morphology may relate to improved surface area and OER performance of PtZrIr

- PtIr: Ir grows epitaxially on Pt, the two catalyst are indistinguishable in Z-contrast images.
- PtZrIr: Ir grows in crystalline “islands” over ZrOx
Collaboration

Partners

- **AFCC** (Subcontractor):
  - Independent evaluation, Short-stack testing, Ex-situ/in-situ characterization, Component integration, Fundamental understanding

- **Dalhousie University** (Subcontractor):
  - High-throughput catalyst synthesis and basic characterization
  - Fully integrated since its inception, during the proposal phase
  - It runs as one single program
  - Results reviewed during weekly scheduled teleconferences and many more unscheduled contacts between participants.

- **Oak Ridge National Lab** (Subcontractor):
  - Fully integrated, provides invaluable feedback and insight into the OER catalyst
  - STEM and EDS analysis fully synchronized with catalyst development

- **Argonne National Lab** (Subcontractor):
  - EXAFS characterization and OER catalyst stability
  - ORR suppression on anode
**Project Relevance**

**Reviewer 1:** this reviewer has never been a strong proponent of this approach... *system-level mitigations* can enable the targets to be exceeded without this technology, it therefore makes the value of this technology questionable.

**Reviewer 2:** “*material based solution*” to improve catalyst performance and durability *will enable simplification* of control and operation of fuel cells.

**Reviewer 3:** project is *highly relevant to DOE hydrogen & fuel cells program* and has the potential to have a big impact on DOE RD&D objectives.

**PI response:** Three OEMs have shown serious interest in evaluating the OEM modified catalysts.

**Reviewer:** Utilizing AFCC to provide gas switching under real-world conditions *allowed for discovery of issues* at low OER catalyst loadings that were not observable under simulated conditions.

**PI:** In the lack of firm DOESUSD targets, OEMs inputs, *AFCCs in particular*, played a crucial role in orienting this project towards the ‘real world’ application.

**Reviewer:** The approach would prove *more universally valuable* if also applied on non-corrosion resistant electrodes such as *dispersed catalysts on carbon*.

**PI:** Within the stability limit of the support, it can be done only for SUSD by suppressing the ORR on the anode. Not for cell reversal where the potential is > 1.7 V.

**Reviewer:** The gas switching and OEM cycling protocols would be especially important to disclose.

**PI:** We have disclosed all the lab procedures in details. This program would benefit if OEMs do the same.

**Reviewer 1:** ....cost of the catalyst may be an issue.

**Reviewer 2:** ....that catalyst durability is improved and the cost of the catalyst is kept low.

**PI:** We have been decreasing the PGM loading throughout the project. The 2014 additives are non-PGM.

**Reviewer:** these catalysts cannot be "*ready for real life*" until NSTF is ready for real life.

**PI:** Fully aware of and agree with. 2014 additives got the OER anode one more step closer to real life readiness. In general, the many achievements of this program have brought the NSTF the closest it has been to practical application.
Summary: Major Findings

• Constructs with additional refractory metals have fulfilled the cell reversal requirement after gas switching and/or gas switching with load cycling within the 2013 Program milestone voltage limit, < 1.7 V, and PGM loading < 0.037 mg/cm².
• Hypothesis that separating the OER catalyst from atomic proximity of Pt may alleviate the impact of gas switching was proven.
• Added benefit of the separating layer is the improved OER activity.
• Fundamental materials studies aimed at understanding the extraordinary durability of the new OER-Pt/NSTF constructs have converged to concluding that stabilizing the Pt and Ir oxides is paramount to increasing reversal endurance.

Future Work and Challenges beyond the end of the Program

General:
• While cell reversal functionality can be achieved, the final OEM determination will be made based on HOR performance under variety of extreme conditions.
• While preserving all the positive attributes, OER/NSTF performance should have no negative impact compared to a conventional dispersed anode.

Specific:
• The constructs with a separating layer open up opportunities for use of wider array of commercially acceptable materials to address both the OER performance and the application issues in general:
  - attempt to reproduce the cell reversal data with commercial grade interlayer materials
• Specific OEM requirements can be more readily addressed by the flexibility offered by the new constructs including the protection of carbon supported catalysts.
Technical Back-Up Slides
SU/SD and OER Catalysts Development Fundamentals

SU/SD Explained

Normal Operation

A

Air

O₂ + 4H⁺ + 4e⁻ → 2 H₂O

H₂ + H⁺ → H₂ + 2e⁻

B

Air Cathode

C + 2H₂O → CO₂ + 4H⁺ + 4e⁻

2H₂O → O₂ + 4H⁺ + 4e⁻

C

Hydrogen

D

Air Anode

O₂ + 4H⁺ + 4e⁻ → 2 H₂O

H₂ → 2 H⁺ + 2e⁻

H₂/Air Front

Stop Start

Basis for Task 1: OER Catalyst

Pt

E/V(rhe) ~0.45 V

j/mA cm⁻²

RuO₂

b/mV

IrO₂

Mol % IrO₂

HOR Uninhibited

δ (HOR) at 500 mA/cm² (mV)

Disk Potential vs. RHE [V]

Basis for Task 2: ORR Inhibition

Bulk Compositions

Pt

Pt₀.₉₅Ta₀.₀₅

Pt₀.₈₈Ta₀.₁₂

Pt₀.₇₉Ta₀.₂₁

Pt₀.₇₅Ta₀.₂₅

Pt₀.₇₂Ta₀.₂₈

Pt₀.₇₁Ta₀.₃

Pt₀.₇Ta₀.₃

Durable Catalysts for Transient Conditions

SU/SD test procedure via Gas Switching between Hydrogen and Air

Reversal durability after 400 mimicked ‘life cycles’ including Gas Switching steps

Standard 50 mg/cm² Pt + 15 mg/cm² IrRu and Modified OER catalyst show (3M lab test)

Modified OER catalyst shows improved durability by a factor > 5

Gas Switching impacts significantly the inherent OER activity of IrRu. Modification of the OER catalyst for improved durability is underway.
Stability correlation to blank cyclic voltammetry

Stability of additives – Zr/Au
- Insight in mechanism of stability increase by additives.
  - Evaluation of additive on Au NSTF elucidates the additive’s basic fingerprint and stability in the cyclic voltammogram (CV)
  - Influence on OER stability probed by comparison with base composition of PtIr 20+15 μg/cm²
- Stability of oxides (Pt, Ir and additive) are the key in OER activity and stability
  - Oxides that are too stable, however, will deactivate the HOR

Zr/Au Voltammetry at 70 °C
- Slight apparent increase in Au oxide feature at 1.4 V. No additional features created
- Extensive potential cycling at 2 mVs⁻¹
  - Redox feature at 1.4/1.1 V increases
  - Feature appears at 0.3 V
    - May be evidence of GDL degradation
- Post mortem analysis:
  - Gold has migrated from anode to membrane
  - Increase in oxide feature is likely a result of roughening
- No Zr dissolution current spotted at any time
XAFS Analyses at Pt, Ir, and Zr Absorption Edges

- Pt-Zr (250 Å)-Ir catalyst and CCM samples after various treatments (Note: NSTF Pd cathode)
- Fitting of near edge region to metal and oxide standards to determine extent of oxidation of Pt, Zr, and Ir
- Atomic-level fitting of extended absorption region (EXAFS) to determine local coordination and bond distances
Summary of XANES Analysis: Pt-Zr-Ir catalyst

• As-prepared
  - Pt metallic; Zr in Pt particles; Pt-Zr particles coated with ZrO₂; Ir either deposited on ZrO₂ or on perylene red whisker

• Conditioned
  - Pt, Ir, and Zr oxidized; Zr shows greatest change in oxidation state; Pt-Zr intermetallic retained

• 200 mA/cm² treatment
  - Zr almost entirely removed from Pt particles; Zr further oxidized, Ir almost fully oxidized to IrO₂

• Gas switching
  - Ir oxide partially reduced (35% metallic); Pt slightly reduced; Zr oxide unchanged

• Cell reversal
  - Zr nearly fully oxidized, Ir fully oxidized, Pt reduced, Zr and Ir are found on the cathode

• Postulated role of Zr interlayer:
  - allows the oxidation of Ir, inhibiting Ir dissolution and loss
  - formation of Pt-Zr surface alloy during deposition inhibits interaction between Pt and Ir